On energy estimators in path integral Monte Carlo simulations: Dependence of accuracy on algorithm

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Two energy estimators, the Barker estimator and the Berne virial estimator, commonly used in path integral simulations of quantum systems are compared with respect to statistical accuracy. It is found that the accuracy of these estimators is strongly affected by the algorithm used. Four common algorithms are considered here: (1) the pure primitive algorithm, (2) the primitive algorithm augmented by whole chain moves, (3) the normal-mode algorithm, and (4) the staging algorithm. The error of the mean of the Barker energy estimator is found to grow as $\sqrt{P}$, where P is the number of discretization points of the quantum paths (or the number of chain particles in the isomorphic classical chain), for all of the algorithms above. The error of the mean of the Berne virial energy estimator is independent of P for algorithms 2, 3, and 4, and increases as $\sqrt{P}$ for algorithm 1. It is concluded that the virial estimator is far more accurate than the Barker estimator for algorithms 2, 3, and 4, and is at least as accurate for algorithm 1. Because the error analysis depends strongly on the temporal correlations in the sequence of values of the energy estimator generated during Monte Carlo or molecular-dynamics simulations, we review the general question of error analysis in simulations.

I. INTRODUCTION

Path integral Monte Carlo based on a discrete representation of the path integral is very useful for simulating quantum and mixed quantum-classical systems.[1] In the discretized approximation of the path integral the partition function of a quantum particle moving in a potential field, $V(x)$, is isomorphic to the partition function of a P particle classical cyclic chain polymer in which each atom is coupled to its two nearest neighbors through harmonic springs and is acted on by an attenuated external potential $V(x)/P$. Physical properties of interest can be expressed as estimators in terms of the coordinates of the classical polymer. Averaging the estimators over the sampled chain configurations gives the ensemble average of the quantum operator.

Two energy estimators are now commonly used: namely the Barker estimator[2] of Eq. (3.1), and the Berne virial estimator of Eqs. (3.2) and (3.8).[3,4] Herman *et al.*[3] showed that the variance of the Barker estimator grows as P, the number of discrete points in the isomorphic chain polymer, and thus becomes less and less accurate as the isomorphic chain is made a more accurate representation of the quantum particle. Because of this, Herman *et al.* proposed a new estimator based on the virial theorem. Both the virial and the Barker estimators give the correct energy, but the variances are different. The variance of the virial estimator is almost independent of P. Hence, the authors state that the virial estimator is superior to the Barker estimator.

The variances calculated analytically by Herman *et al.* are

$$\sigma_0^2 = \frac{1}{S} \sum_{j=1}^{S} (\epsilon_j - \bar{\epsilon})^2 \tag{1.1}$$

where ϵ_j is the value of the energy estimator after move j, and

the averaging is done over the total number of moves, S, in a Monte Carlo run. This definition of the variance provides an accurate determination of the error only if the sequence of values $\{\epsilon_j\}$ are uncorrelated, an assumption that should be supported by a correlation analysis. A series of configurations in the Metropolis importance sampling is usually not statistically independent but is correlated; the error estimates should thus account for this correlation. To compare the convergence of the two energy estimators the correlation lengths should be evaluated and included in the standard deviation in the mean. Giansanti and Jacucci[5] have shown that the correlation length of the "virial estimator" displays a more than linear growth with P while the correlation length of the "estimator" increases weakly with P, and they conclude that the virial estimator is not superior to the Barker estimator.

In this paper we show that the error is very strongly dependent on the Monte Carlo (or molecular dynamics) algorithm used. Four common algorithms are considered here.

(1) The pure primitive algorithm, where a move for each bead is sampled independently and accepted or rejected using the usual Metropolis importance sampling scheme with the pure primitive action.[2]

(2) The primitive algorithm augmented by whole chain moves, where in addition to moving each bead, a move of the center of mass of the whole chain is attempted and accepted or rejected based on the Metropolis importance sampling scheme again using the primitive action.[1]

(3) The normal-mode algorithm, where the part of the primitive action corresponding to the kinetic energy operator; that is, the harmonic spring part, is resolved into normal modes. Each normal mode is sampled using a Box–Mueller technique, and the result is accepted or rejected based on the usual importance sampling criteria. Because one of the nor-

mal modes is the center-of-mass position, this method incorporates the advantages of the preceding method.[3]

(4) The Ceperley–Pollock staging algorithm,[6] where segments of the chain are moved using a Levy-walk algorithm. This technique leads to greater amoeba-like mobility of the chain.

When Monte Carlo (MC) is performed using method 1, both the Barker estimator and the virial estimator have errors that grow with the number of beads on the chain, and are equally bad in predicting the kinetic energy, as first pointed out by Giansanti and Jacucci.[5] When MC is performed using methods 2, 3, and 4 the chain is able to move more freely over the potential-energy surface so that the correlation length of the virial estimator is significantly reduced and is no longer strongly dependent on P. Now the virial estimator is clearly superior to the Barker estimator. Correlation lengths depend not only on the form of the estimator but also on the Monte Carlo algorithm used. We conclude that when optimum methods are used to move the chain the virial estimator is clearly superior to the Barker estimator.

II. ERROR ESTIMATES FOR CORRELATED DATA

In this section we summarize how error estimates are made for averages over the consecutive steps in molecular-dynamics (MD) and MC simulations which are correlated. This subject has received considerable attention lately.[7]

If a run of length $S = nN$ is divided into N blocks with n steps per block, $X_\alpha^{(i)}$ denotes the value of the estimator of a macroscopic property at the time steps $\{\alpha = 1,2,...,n\}$ of the ith block $\{i = 1,2,...,N\}$, $\overline{X}_i$ denotes the average over the ith block, $\overline{X}_i = (1/n)\Sigma_{\alpha=1}^n X_\alpha^{(i)}$ and $\overline{\overline{X}} = (1/N)\Sigma_{i=1}^N \overline{X}_i$ denote the average over all blocks, that is, over all the data; then the standard deviation of the block average is, for $N \gg 1$,

$$\sigma^2 = \frac{1}{N}\sum_{i=1}^N (\overline{X}_i - \overline{\overline{X}})^2, \tag{2.1}$$

and the error in the mean, Δ is

$$\Delta = \sqrt{\sigma^2/N}. \tag{2.2}$$

It is a simple matter to show that Δ can be expressed as

$$\Delta^2 = \Delta_0^2\left[1 + \frac{2}{n}\sum_{k=1}^{n-1}(n-k)C(k)\right], \tag{2.3}$$

where

$$\Delta_0^2 \equiv \frac{1}{n^2N^2}\sum_{i=1}^N\sum_{\alpha=1}^n (X_\alpha^{(i)} - \overline{\overline{X}})^2 \tag{2.4}$$

is the standard error in the mean of the uncorrelated data defined in Eq. (1.1), and

$$C(k) = \left(\frac{n}{n-k}\right)\frac{\Sigma_{\alpha=1}^{n-k}\langle\delta X_\alpha \delta X_{\alpha+k}\rangle}{\Sigma_{\alpha=1}^n\langle\delta X_\alpha \delta X_\alpha\rangle} \tag{2.5}$$

is the normalized autocorrelation function of the fluctuations, $\delta X_\alpha^{(i)} = X_\alpha^{(i)} - \overline{X}$.

It is of considerable interest to determine how this depends on the length of the run, $S = nN$, and on the size of the blocks used in the averaging process. To gain some insight into this behavior we consider the following three models.

Case (*a*). There are no correlations between successive

fluctuations in each block. Then $C(k) = \delta_{k,0}$. Substitution of this into Eq. (2.3) then gives

$$\Delta_2 = \Delta_0^2, \tag{2.6}$$

where Δ_0^2 is the one standard deviation error in the mean of uncorrelated data [see Eq. (1.1)].

Case (*b*). All fluctuations are completely correlated for n_c steps and uncorrelated thereafter; that is, $C(k) = \theta(n_c - k)$. Substitution of this into Eq. (2.3) yields

$$\Delta^2 = \begin{cases} n\Delta_0^2, & n \leqslant n_c \\ \Delta_0^2[(1 + 2n_c) - n_c(n_c + 1)/n], & n > n_c \end{cases} \tag{2.7}$$

This increases linearly with n for $n \leqslant n_c$ and saturates at $2n_c\Delta_0^2$ for $n \gg n_c$.

Case (*c*). The correlations die off exponentially with the correlation function $C(k) = \exp(-\lambda k)$, where $\lambda = 1/n_c$. Substitution of this into Eq. (2.3) yields

$$\Delta^2 = \Delta_0^2\left\{1 + \frac{2}{n}\left[\frac{(n - e^{-\lambda(n-1)})}{(e^\lambda - 1)} - \frac{(1 - e^{-\lambda(n-1)})}{(e^\lambda - 1)^2}\right]\right\}. \tag{2.8}$$

For $n \gg n_c$ it follows that

$$\Delta^2 = \Delta_0^2 \coth\left(\frac{1}{2n_c}\right). \tag{2.9}$$

This result shows that for $n \gg n_c$ the error of the estimator depends on the correlation time n_c of the fluctuations. If in addition $n_c \gg 1$, Eq. (2.8) reduces to

$$\Delta^2 = (2n_c)\Delta_0^2, \tag{2.10}$$

in which case the variance of the estimator is a linear function of the correlation time. In general, Eq. (2.3) reduces to Eq. (2.10) for $n \gg n_c$ if $n_c \equiv \Sigma_{k=1}^\infty C(k)$ and $\Sigma_{k=1}^\infty kC(k)$ are finite.

A good example of the foregoing is furnished by a Monte Carlo simulation (using staging) of a linear harmonic oscillator. Figure 1 shows a record of the virial energy estimator (see the next section). The whole run consists of $S = 10^4$ passes. For this data $\Delta_0 = 6.74\times10^{-3}$. The data is divided into N blocks of n steps each and Δ^2 is determined using Eq. (2.2). This is plotted in Fig. 2 as a function of block size n for fixed $S = nN$, and from this the saturated error is found to be $\Delta = 1.25\times10^{-2}$. Assuming that the correlation function decays exponentially and using Eq. (2.9) allows us to estimate the correlation length as $n_c = 1.67$. A plot of Δ determined from Eq. (2.3) is in very good agreement with Δ determined from Eq. (2.8), indicating that the correlation function is exponential.

The preceding evaluation of the error is based on determining how Δ depends on the number of steps per block and computing the error from the saturated value of Δ thus obtained. An alternative approach is to evaluate the correlation length from direct numerical determination of the correlation function $C(k)$ from the energy record using Eq. (2.5). The result shown in Fig. 3 appears to be an exponential function of k, as in case (c) above, with $n_c = 1.71$. The value of the square error Δ^2 for $n \gg n_c$ is then determined from Eq. (2.9). Substitution of $\Delta_0 = 6.74\times10^{-3}$ gives
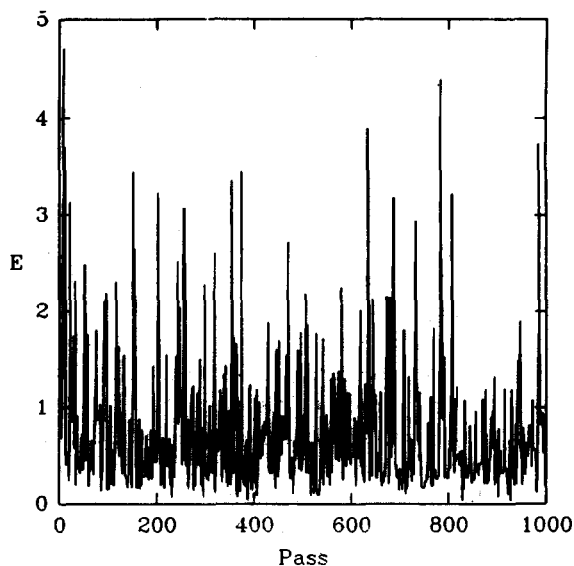
FIG. 1. A part of the record of the virial energy estimator consisting of 10^3 steps. The system simulated is LHO defined above.

$\Delta = 1.26 \times 10^{-2}$, which agrees with the saturated value of Δ^2 determined above.

Usually, plotting the block error is an economical way to do error analysis, although direct determination of the correlation function allows the determination of $n_c = \Sigma_{k=1}^{\infty} C(k)$ directly, and together with Eq. (2.10) allows one to calculate the error Δ.

III. THE ENERGY ESTIMATORS

The two energy estimators mentioned in the Introduction are the Barker energy estimator ϵ_P^B and the Berne virial energy estimator ϵ_P^V:
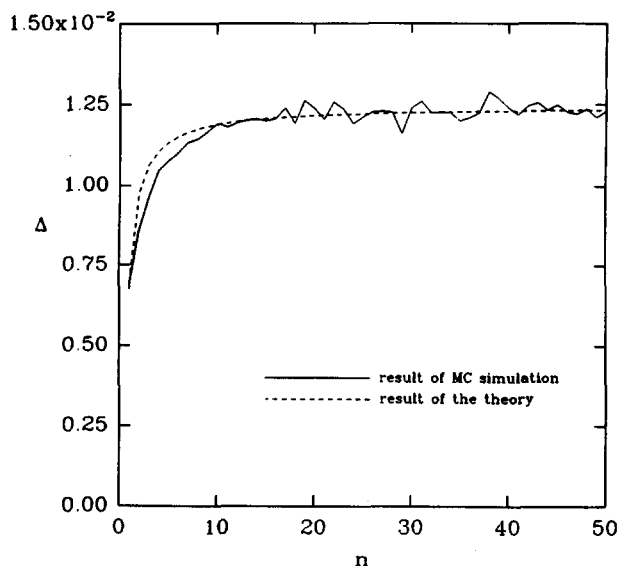

FIG. 2. A plot of the error Δ vs the block size n. The solid curve is for the virial estimator of a staging MC run of a LHO with parameters defined above and 10 beads. For this case, Δ_0 is 6.74×10^{-3} and the saturated value is $\Delta = 1.25 \times 10^{-2}$. Assuming that the correlation function decays exponentially, we estimate the correlation length $n_c = 1.67$ using Eq. (2.9). The dashed curve is the plot predicted using Eq. (2.8) with the same correlation length n_c.
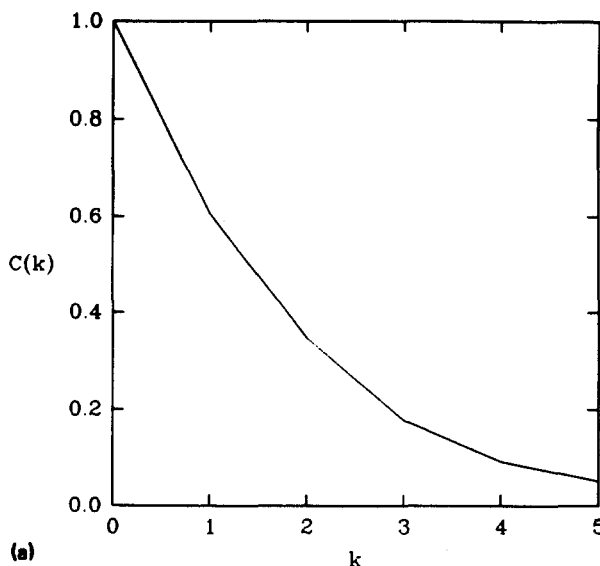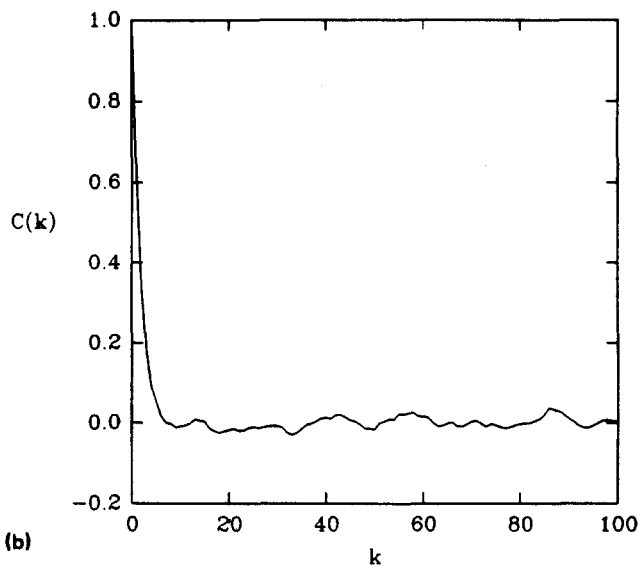
FIG. 3. The normalized autocorrelation function $C(k)$ of the same set of data as was used in Fig. 2. (a) $k = 1, 5$; (b) $k = 1, 100$.

$$\epsilon_P^B = \frac{Pd}{2\beta} - \frac{mP}{2\hbar^2\beta^2} \sum_{t=1}^{P} (x_t - x_{t-1})^2 + \frac{1}{P} \sum_{t=1}^{P} V(x_t),$$
(3.1)

$$\epsilon_P^V = \frac{1}{P} \sum_{t=1}^{P} \left[V(x_t) + \frac{1}{2} x_t \cdot \frac{\partial V(x_t)}{\partial x_t} \right],$$
(3.2)

where ϵ_P^V as written is for a particle moving in a localizing potential, subscript P denotes the number of discretization points on the chain, and d is the dimensionality of the system. Although the averages of these two estimators are identical ($\langle \epsilon_P^B \rangle = \langle \epsilon_P^V \rangle$), in general, the error Δ_0, defined in Eq. (2.4), of the Barker estimator grows linearly with $\sqrt{P}$, in contrast to the error for the virial estimator which does not depend strongly on P. Thus, based on the assumption of uncorrelated data, and hence the use of Δ_0 for the error analysis, the virial estimator is preferred because it has less error associated with it. In MC and MD simulations the data is correlated, and one must use the foregoing analysis to deter-

mine the error Δ associated with the two estimators. Giansanti and Jacucci[5] have shown that for Monte Carlo simulations based on the pure primitive algorithm the correlation length associated with ϵ_P^V grows with P, whereas the correlation length associated with ϵ_P^B varies slowly with P. When these results are substituted into Eq. (2.10) it is clear that the two estimators both have errors that grow as $\sqrt{P}$. Consequently, as P is increased to ensure convergence of the discrete path integral to the exact result, the errors in both of these estimators grow without bound. In the remaining part of this paper we show that if commonly used Monte Carlo algorithms are used in place of the pure primitive algorithm, the error in the virial estimator does not grow with $\sqrt{P}$, whereas the error in the Barker estimator still grows with $\sqrt{P}$, and is thus very inaccurate.

In path integral Monte Carlo one samples the configurations according to the density matrix,[1] the relevant part of which is $e^{-\beta H}$ where the Euclidean action is

$$H = \frac{mP}{2\beta^2\hbar^2} \sum_{t=1}^{P} (x_t - x_{t+1})^2 + \frac{1}{P} \sum_{t=1}^{P} V(x_t). \quad (3.3)$$

For simplicity of comparison, we drop the pure potential part $\Sigma_{t=1}^{P} V(x_t)/P$ and concentrate on the kinetic part of the energy estimators:

$$\alpha_P^P = \frac{Pd}{2\beta} - \frac{mP}{2\beta^2\hbar^2} \sum_{t=1}^{P} (x_t - x_{t+1})^2, \quad (3.4)$$

$$\alpha_P^V = \frac{1}{2P} \sum_{t=1}^{P} x_t \frac{\partial V(x_t)}{\partial x_t}. \quad (3.5)$$

Obviously, the Barker kinetic energy estimator α_P^P is related to the relative position of the beads; while the virial kinetic energy estimator α_P^V is related to the gradient of potential felt by each bead. As we increase the number of beads, the harmonic coupling $mP/2\hbar^2\beta^2$ between the beads grows with P, and the chain becomes stiffer.[1] In the standard Metropolis importance sampling using the pure primitive algorithm, beads are moved individually, and since the first term of Eq. (3.3) allows only small moves of the individual beads and thereby only small excursions of the average potential, $\Sigma_{t=1}^{P} V(x_t)/P$, and of the average virial, $\Sigma_{t=1}^{P} x_t \cdot [\partial V(x_t)/\partial x_t]/P$. By the same token, because the moves that are being sampled are controlled by the first term of the action on the right-hand side of Eq. (3.3), we expect large changes of the Barker estimator, Eq. (3.4), per move. These effects are expected to introduce large correlation lengths into the virial estimator, correlation lengths that grow with P because the chain becomes stiffer, but should leave the correlation length of the Barker estimator relatively insensitive to P, a finding first observed by Giansanti and Jacucci. If the pure primitive algorithm is augmented by randomly moving the chain as one stiff unit, the Monte Carlo moves will then not only change the position of the individual beads but will also move all beads together by a much larger displacement than would be allowed by stiff harmonic bonds in the action. This whole body move does not change the first term of the action but does allow large changes in the potential and the virial. Such moves should therefore have no effect on the correlation time of the Barker estimator, but

should decrease the correlation time of the virial estimator enormously, as will now be shown. In general, movement of the whole chain generates more efficient sampling, and has often been used in path integral simulations of liquids.

The Monte Carlo simulations of the linear harmonic oscillator with potential $V = m\omega^2 x^2/2$ reported below use the following parameters: $\beta m\omega^2/2 = 1.0$ and $\beta\hbar\omega = 3.0$. All runs are performed for $S = 10^4$ moves. The step sizes and the number of moving beads are adjusted to reach an acceptance rate of approximately 50%. In all the plots, the squares ($\square$) indicate the data for the Barker estimator and the circles ($\bigcirc$) indicate the data for the virial estimator or when applicable the generalized virial estimator. The correlation length n_c is determined from the exponential decay of the respective autocorrelation function. The error in the mean is taken to be the saturated value of Δ using Eq. (2.9).

In Fig. 4 the step size of the whole chain is gradually increased. The correlation length of the virial estimator decreases drastically and the correlation length of the Barker estimator is not very much affected as anticipated above. Therefore, the MC moves of the whole chain provide enough mobility to reduce the correlation length and the error of the virial estimator.

Figure 5 shows how the error and the correlation length of the Barker estimator and the virial estimator vary with the number of beads, P, in the above MC simulation with whole chain moves. Clearly, the Barker estimator has an error which increases with $\sqrt{P}$, and the virial estimator has an error that does not increase with $\sqrt{P}$. Thus, simply by incorporating whole body moves in the algorithm, a common technique, the virial estimator now becomes superior to the Barker estimator.
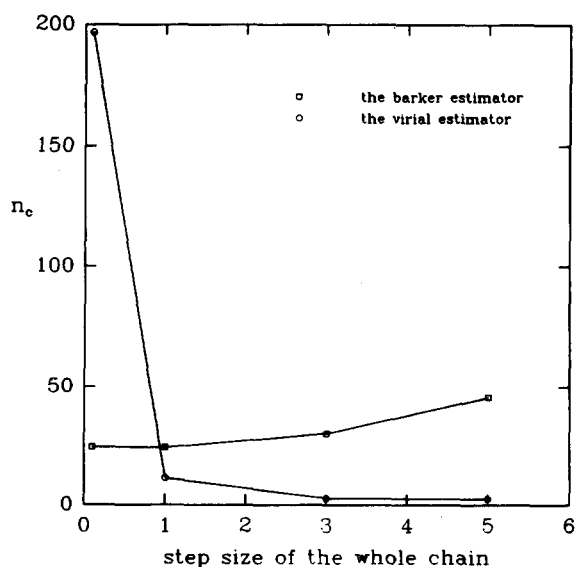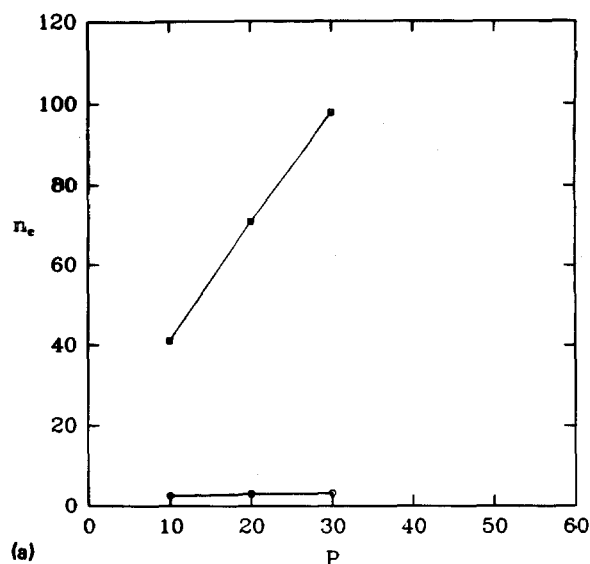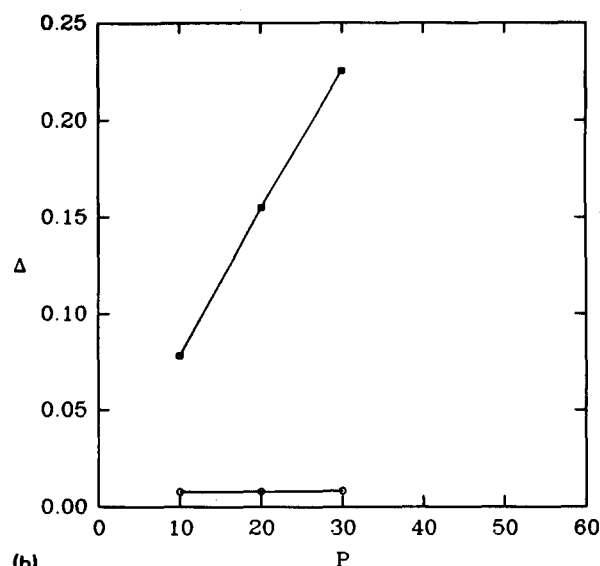

FIG. 4. The correlation length n_c of the Barker estimator and the virial estimator as a function of the step size of the whole body moves in the augmented primitive algorithm. The system simulated is the LHO defined above. The squares indicate the data for the Barker estimator and the circles indicate that for the virial estimator.
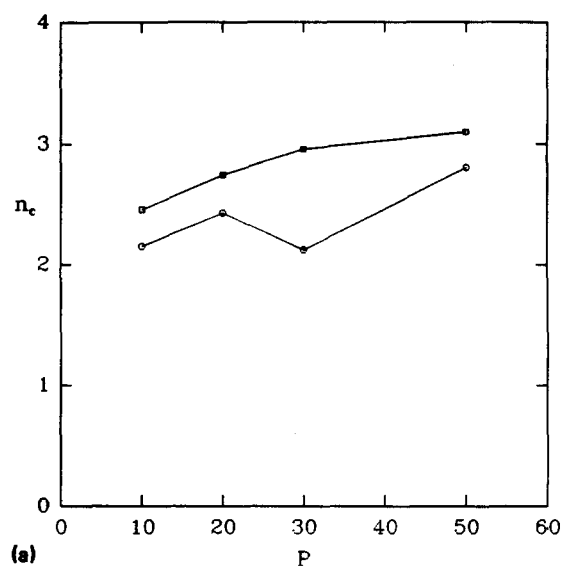
$$H = \frac{mP}{2\beta^2\hbar^2} \sum_k \left\{ 2\left\{ 1 - \cos\left(\frac{\pi k}{P}\right) \right\} \right\} Q_k^2$$

$$+ \frac{1}{P} \sum_{t=1}^{P} V(x_t(\{Q_k\})). \tag{3.7}$$

New steps are generated by the direct sampling of Q_k from the Gaussian distribution of the diagonal first term in Eq. (3.7) and random movement of x_0. This allows for larger moves of low-frequency modes than would be allowed in the primitive algorithm. Figure 6 compares how the correlation length and error of the Barker and the virial estimators depend on P for the normal-mode simulation. Clearly, the behavior here is similar to the results shown in Fig. 5. Again, the virial estimator is superior to the Barker estimator.

FIG. 5. (a) The correlation length n_c vs the number of beads, for the Barker estimator and the virial estimator using the primitive algorithm with augmented whole chain moves where the step size is chosen to yield an acceptance probability of 50%. The system simulated is the LHO defined above. (b) The error Δ in the mean vs P for the same run in (a). The squares indicate the data for the Barker estimator and the circles indicate that for the virial estimator.

It is of interest to investigate the normal-mode method. The zero-frequency normal modes of the chain correspond to translations and/or rotations and should lead to short correlation times in the virial estimator as above. The real coordinates of the beads $\{x_t\}$ are transformed to the Fourier coordinates Q_k according to the following transformation:

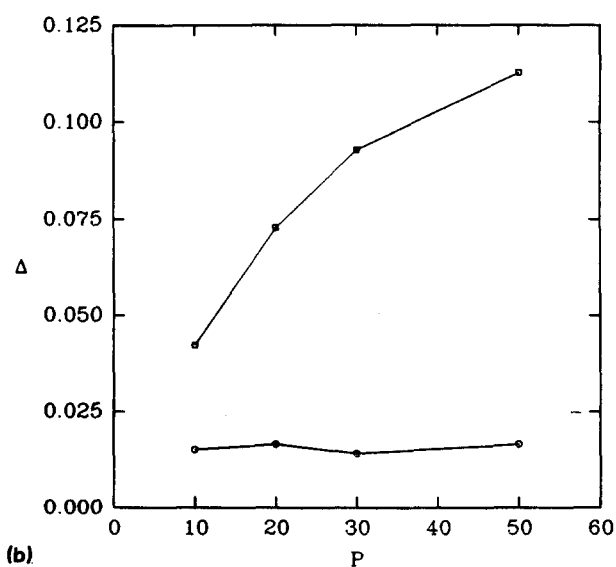$$x_t = x_0 + (2/n)^{1/2} \sum_k \sin(\pi k t / P) Q_k. \tag{3.6}$$

With the help of this transformation, the kinetic part of S is diagonalized, and

FIG. 6. (a) The correlation length n_c vs the number of beads, for the Barker estimator and the virial estimator using the normal-mode MC algorithm. The system simulated is the LHO defined above. (b) The error Δ in the mean vs P for the same run in (a). The squares indicate the data for the Barker estimator and the circles indicate that for the virial estimator.

In the staging algorithm moves of segments of the chain are generated from the first term of the action, S, in Eq. (3.3) using a Levy walk, and are accepted or rejected according to the second term.[8] This procedure is equivalent to the scheme devised by Ceperley and Pollock[9,6] with the drift terms omitted. The stiffness of the chain is thereby removed, making the chain much more mobile than in the primitive algorithm, and thus allowing the potential energy and the virial estimator to fluctuate by large amounts from one staging pass to another. Once again we expect that the correlation length of the virial estimator will be very short. In Fig. 7 the results for the linear harmonic oscillator (LHO) potential show that for the staging algorithm the virial estimator is again more accurate than the Barker estimator.

It is of interest to see if anharmonicity will change these conclusions. Figure 8 shows the results using staging MC on a quartic oscillator $V = m\omega^2 (x^2 + x^4/2)/2$, where β, m, and ω take the same values as for the LHO. Again, Δ^β grows with $\sqrt{P}$ but Δ^V is essentially constant.

In all of the foregoing, only true bound-state systems are considered; that is, systems confined by a localizing potential like the harmonic or quartic potentials. The virial estimator for unbound systems moving in periodic boundary conditions can be expressed as [4]
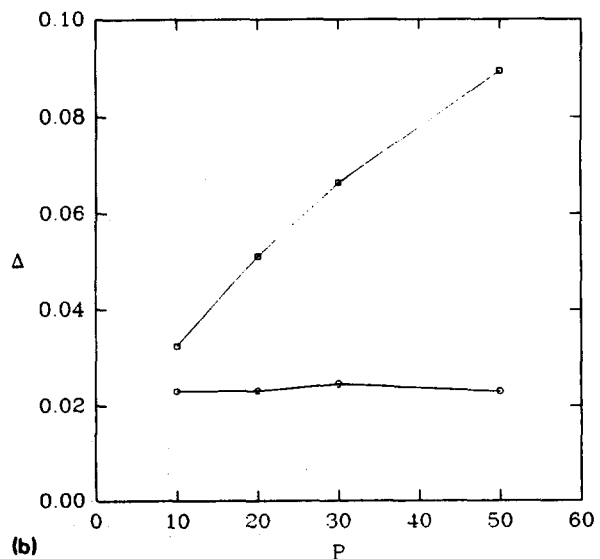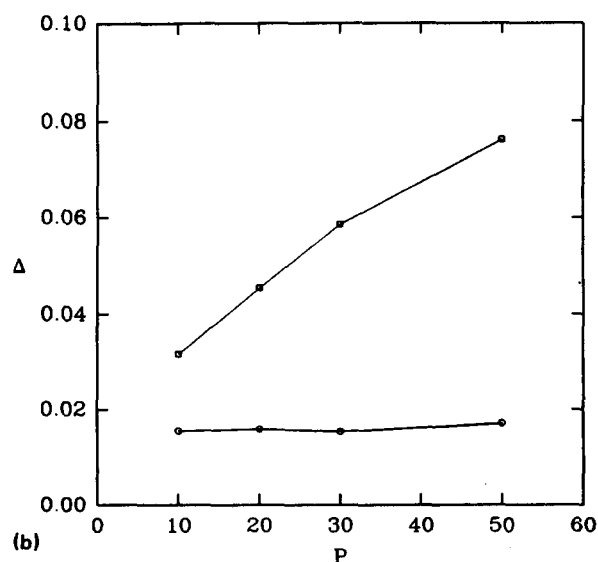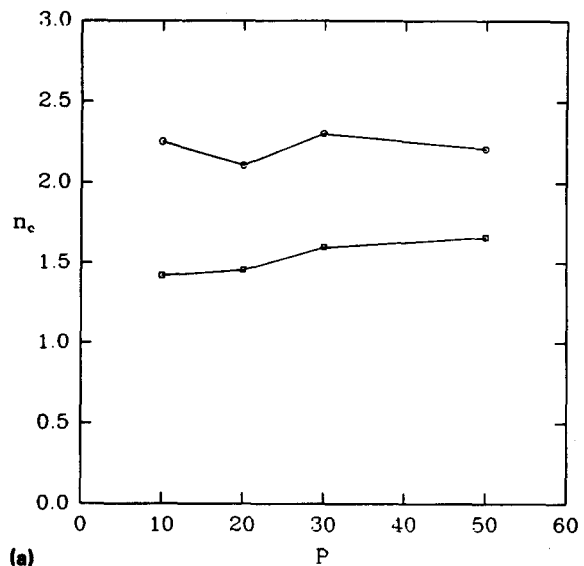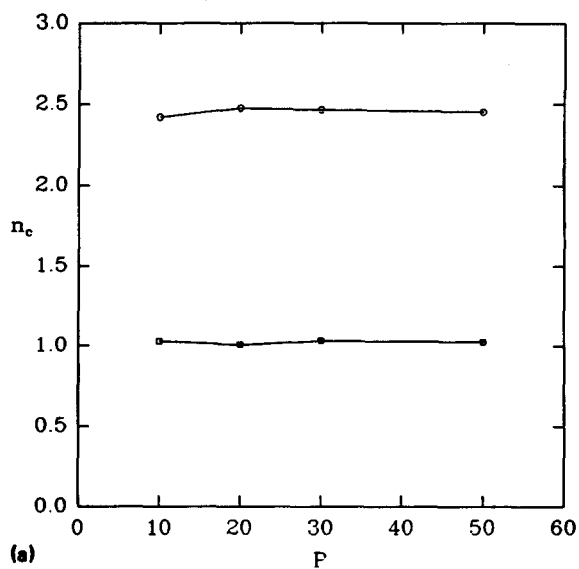

(a)

(b)

FIG. 7. (a) The correlation length n_c vs the number of beads, for the Barker estimator and the virial estimator using the staging MC algorithm. The system simulated is the LHO defined above. (b) The error Δ in the mean vs P for the same run in (a). The squares indicate the data for the Barker estimator and the circles indicate that for the virial estimator.

(a)

(b)

FIG. 8. (a) The correlation length n_c vs the number of beads, for the Barker estimator and the virial estimator using the staging MC algorithm. The system simulated is a quartic oscillator $V = m\omega^2 [x^2 + (1/2)x^4]$ where β, m, and ω take the same values as the LHO defined above. (b) The error Δ in the mean vs P for the same run in (a). The squares indicate the data for the Barker estimator and the circles indicate that for the virial estimator.

$$\epsilon_P^{VG} = \frac{d}{2\beta} + \frac{1}{P} \sum_{t=1}^{P} \left[V(x_t) + \frac{1}{2}(x_t - x_P) \frac{\partial V(x_t)}{\partial x_t} \right],$$

(3.8)

where the superscript VG denotes the generalized virial estimator. The first term $d/2\beta$ gives the exact kinetical energy of a classical particle; the second term gives the average potential energy; and the third term gives the quantum correction to the kinetic energy. This last term is related to the change of the potential over the size of the isomophic chain. Simple algebra shows that this form reduces to ϵ_P^V for bound systems, and is thus also applicable to bound systems like the harmonic and quartic systems.

We apply this generalized virial estimator ϵ_P^{VG} to an unbound periodic potential $V(x) = \cos(x)$ of period of 2π. The periodicity is simulated by requiring that once the bead drifts out of the boundary, it enters through the opposite boundary. The effect of periodicity will become more dramatic as the temperature is lowered, because the chain will then begin to sense the whole periodic interval. Because the temperature is reasonably high here, no attempt is made to incorporate the periodicity into the short-time propagator, although this can be done for the normal-mode and staging algorithms. Again the comparison of the two estimators
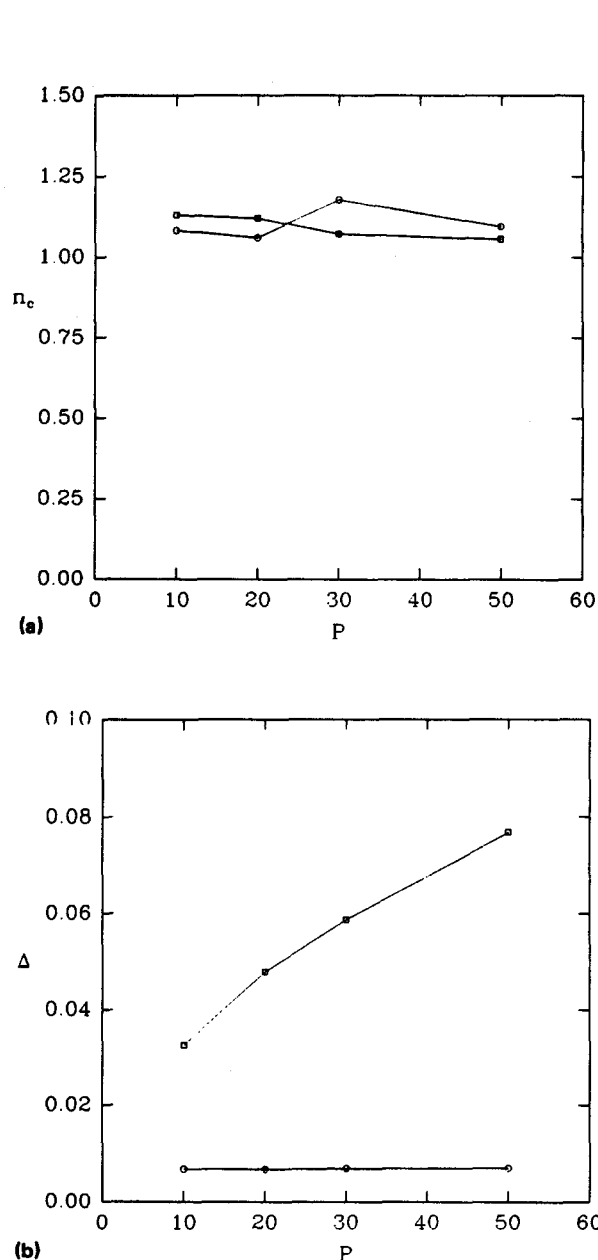

FIG. 9. (a) The correlation length n_c vs the number of beads, for the Barker estimator and the generalized virial estimator using the staging MC algorithm. The system simulated is the LHO defined above. (b) The error Δ in the mean vs P for the same run in (a). The squares indicate the data for the Barker estimator and the circles indicate that for the virial estimator.
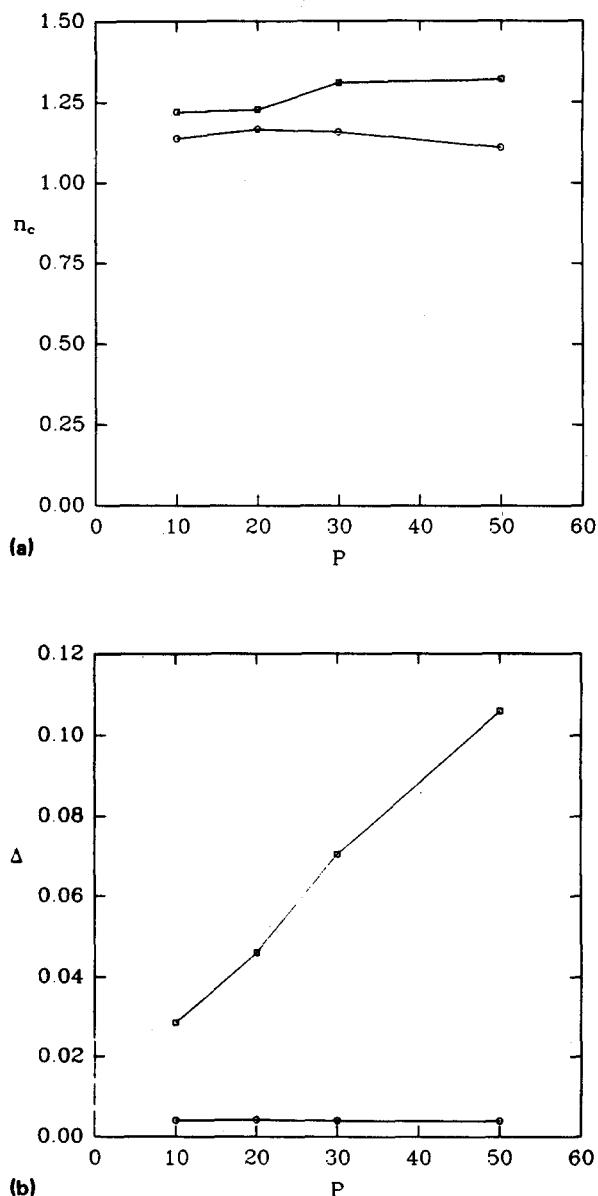
FIG. 10. (a) The correlation length n_c vs the number of beads, for the Barker estimator and the generalized virial estimator using the staging MC algorithm. The system simulated is an unbound potential with periodic boundary condition. We adopt a cosine potential $V(x) = \cos(X)$ with $\beta = 1.0$, $\hbar = 1.0$, mass $= 1.0$. The chain is confined in the domain of one period from 0 to 2π. (b) The error Δ in the mean vs P for the same run in (a). The squares indicate the data for the Barker estimator and the circles indicate that for the virial estimator.

shows that Δ increases with $\sqrt{P}$ for the Barker estimator and is independent for the virial estimator.

In conclusion, we have investigated four different Monte Carlo algorithms: the pure primitive MC, the primitive MC with whole chain moves, the normal-mode MC, and the staging MC. The correlation length not only depends on the form of the estimator, but also on the algorithm. After the correlation length is properly taken into account, the results of the statistical error analysis strongly support the conclusion that the error of the pure Barker estimator grows with the $\sqrt{P}$ while the error of the virial estimator does not depend on P. In this sense, the virial estimator has clear advantages over the Barker estimator as was originally suggested by Berne et al. Only when a pure primitive algorithm is used on a true bound system, as in the paper of Giansanti and Jacucci[5] is there no advantage to using it. For simulations on systems with periodic boundary conditions we have shown that the error in the generalized virial estimator also is not dependent on P, whereas for the Barker estimator the

error grows as $\sqrt{P}$ as before. In most modern Monte Carlo work, either staging or whole body moves are made, in which case the virial estimators ϵ_P^V and ϵ_P^{VG} are clearly superior to the Barker estimator ϵ_P^B.

ACKNOWLEDGMENT

[1] B. J. Berne and D. Thirumalai, Annu. Rev. Phys. Chem. **37**, 401 (1986).
[2] J. Barker, J. Chem. Phys. **70**, 2914 (1979).
[3] M. F. Herman, E. J. Bruskin, and B. J. Berne, J. Chem. Phys. **76**, 5150 (1982).
[4] M. Parrinello and A. Rahman, J. Chem. Phys. **80**, 861 (1984).
[5] A. Giansanti and G. Jacucci, J. Chem. Phys. **89**, 7454 (1988).
[6] E. L. Pollock and D. M. Ceperley, Phys. Rev. B **30**, 2555 (1984).
[7] M. P. Allen and D. J. Tildesley, *Computer Simulation in Liquids* (Oxford University Press, Oxford, 1987).
[8] D. F. Coker, B. J. Berne, and D. Thirumalai, J. Chem. Phys. **86**, 5689 (1987).
[9] D. M. Ceperley and E. L. Pollock, Phys. Rev. Lett. **56**, 351 (1986).